



(43) International Publication Date  
6 December 2001 (06.12.2001)

PCT

(10) International Publication Number  
**WO 01/92354 A2**

(51) International Patent Classification<sup>7</sup>: **C08F 210/00**

(21) International Application Number: **PCT/US01/17626**

(22) International Filing Date: **31 May 2001 (31.05.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
60/208,087 31 May 2000 (31.05.2000) US  
60/211,601 15 June 2000 (15.06.2000) US  
60/214,036 23 June 2000 (23.06.2000) US  
60/264,537 25 January 2001 (25.01.2001) US

(71) Applicant (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JOHNSON, Lynda,**

**K.** [US/US]; 707 Burnley Road, Wilmington, DE 19803 (US). **WANG, Lin** [US/US]; 112 Brook Run, Hockessin, DE 19707 (US). **MCCORD, Elizabeth, F.** [US/US]; 514 Hemlock Drive, Hockessin, DE 19707 (US).

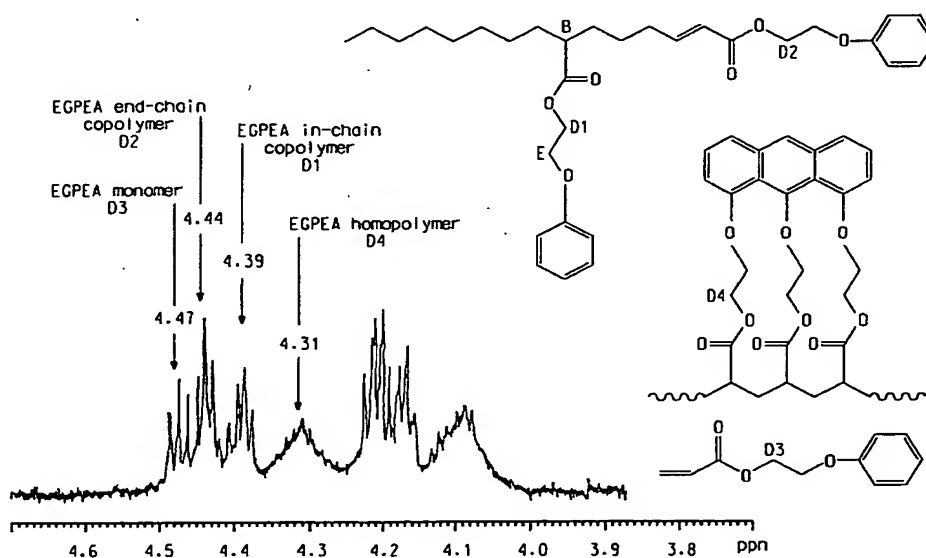
(74) Agent: **LERMAN, Bart, E.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: **COPOLYMERS OF ETHYLENE AND SELECTED ACRYLATE ESTERS**



(57) Abstract: In the copolymerization of ethylene and acrylate esters, the use of selected acrylate esters suppresses the formation of acrylate ester homopolymer, and/or allows the rapid analysis by <sup>1</sup>H-NMR of the amount of homopolymer by product present in the copolymer, both aids in manufacturing high quality copolymers. Useful such acrylates include hexyl acrylate, 3,5,5-trimethylhexyl acrylate, 2-phenoxyethyl acrylate and 2-phenylethyl acrylate. The polymers are useful for films and molding resins.

WO 01/92354 A2



**Published:**

— without international search report and to be republished  
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

## TITLE

COPOLYMERS OF ETHYLENE AND SELECTED ACRYLATE ESTERS

## FIELD OF THE INVENTION

Copolymers of ethylene and selected acrylate esters may be readily analyzed for the presence of acrylate ester homopolymers, thereby rendering quality control during their manufacture cheaper and faster. A process for copolymer manufacture is also disclosed. The copolymers are useful for films and as molding resins.

## TECHNICAL BACKGROUND

Recently it has become possible to prepare copolymers of olefins, especially ethylene, with acrylate esters, using late transition metal polymerization catalysts. See for instance US5866663, and S. D. Ittel, et al., Chem. Rev., vol. 100, p. 1169-1203 (2000), both of which are incorporated by reference herein for all purposes as if fully set forth.

One problem that sometimes occurs in these polymerizations is the formation of the desired copolymer together with some amount of a homopolymer of the acrylate ester(s) (more than one ester may be present). This is believed to arise because acrylate esters also undergo facile free radical polymerizations, which can occur in the same system as the transition metal catalyzed copolymerization with ethylene. While analysis of the amount of homopolymer present and also the amount of ester group present in the copolymer can be done by  $^{13}\text{C}$ -NMR spectroscopy, such analyses are usually very time consuming, resulting in long delays between sampling and results, meaning adjustments to the manufacturing system to minimize homopolymer formation or adjust the level of acrylate incorporation may be delayed a long time, an obvious disadvantage. This together with the high cost of the analysis itself is a drawback for making these copolymers by coordination polymerization.

Therefore homo- and copolymer mixtures that are readily analyzed, or the use of acrylate esters which do not homopolymerize readily under coordination polymerization conditions, are desirable.

#### SUMMARY OF THE INVENTION

5 This invention concerns a process for the manufacture of a copolymer, comprising the step of contacting, under polymerization conditions, a monomer component comprising ethylene and one or more acrylate esters (and optionally one or  
10 more other polymerizable olefins), and a polymerization catalyst system containing a transition metal, wherein said one or more acrylate esters comprises a compound of the formula  $H_2C=CHC(O)OR^1$ , wherein:

$R^1$  is  $-CH_2CH_2X$ , an n-alkyl containing 6 or more carbon  
15 atoms, or  $-CH_2R^2$ ;

$X$  is aryl, substituted aryl, hydrocarbyloxy, substituted hydrocarbyloxy, fluoro or fluoroalkyl; and

$R^2$  is an alkyl containing at least one quaternary carbon atom, or having a grouping within  $R^2$  having an  $E_s$  of about  
20 -1.0 or less, or both.

This invention also concerns a copolymer of ethylene, one or more acrylate esters of the formula  $H_2C=CHC(O)OR^1$  (and optionally one or more other copolymerizable monomers), provided that said acrylate esters are about 0.1 to about 30  
25 mole percent of the total number of all repeat units in said copolymer, wherein:

$R^1$  is  $-(CH_2CH_2)X$ , n-alkyl containing 6 or more carbon atoms, or  $-CH_2R^2$ ;

$X$  is aryl, substituted aryl, hydrocarbyloxy, substituted  
30 hydrocarbyloxy, fluoro, or fluoroalkyl; and

$R^2$  is alkyl containing at least one quaternary carbon atom, or having a grouping within  $R^2$  having an  $E_s$  of about -1.0 or less, or both.

These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following detailed description. It is to be appreciated that certain features of the invention which are, for clarity, described below in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombination.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the  $^1\text{H}$ -NMR spectrum of a mixture of an EGPEA homopolymer in a mixture with an EGPEA copolymer with ethylene, produced as described in Example 1 while making the copolymer with a nickel containing olefin polymerization catalyst. The assignments of some of the various peaks are shown.

Figure 2 shows a typical  $^1\text{H}$ -NMR of the polymer product from copolymerization of ethylene and methyl acrylate using a nickel containing polymerization catalyst. There is both copolymer and homopolymer present. The homopolymer peak partially lies under a copolymer peak, and the black shaded portion is an illustration (probably not accurate) showing the actual size of the homopolymer peak.

Figure 3 shows a typical  $^1\text{H}$ -NMR of the polymer product from copolymerization of ethylene and n-hexyl acrylate using a nickel containing polymerization catalyst. There is both copolymer and homopolymer present. The homopolymer peak partially lies under a copolymer peak, but it is easier to estimate the amount of homopolymer present than in the methyl acrylate case.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Herein certain terms are used:

By a "quaternary carbon atom" is meant a carbon atom which is bound to 4 other carbon atoms. An example of a quaternary carbon atom is found in the neopentyl group,  $-\text{CH}_2\text{C}(\text{CH}_3)_3$ .

5 By "aryl" is meant a monovalent group in which the free valence is to a carbon atom of an aromatic ring. The aromatic ring may be a carbocyclic ring or a heterocyclic ring. The aryl group may have one or more aromatic rings, which may be fused, connected by single bonds or other groups.

10 A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. As examples of hydrocarbyls may be mentioned unsubstituted alkyls, cycloalkyls and aryls. If not otherwise stated, it is preferred that hydrocarbyl groups (and alkyl groups) herein contain 1 to about 30 carbon atoms.

15 By a "fluoroalkyl" group is meant an alkyl group substituted with one or more fluorine atoms (and may be perfluoroalkyl). Preferably there is at least one fluorine atom alpha or beta, more preferably alpha, to the free valence of the alkyl group.

20 By "substituted" herein is meant a group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. Included in the meaning of "substituted" are heteroaromatic rings. In substituted groups all of the hydrogens (which may be present) may be substituted, as in trifluoromethyl.

30 By "(inert) functional group" herein is meant a group which is inert under the process conditions to which the compound containing the group is subjected. That is, the functional groups do not substantially interfere with any process described herein that the compound in which they are

present may take part in. Examples of functional groups include halo (fluoro, chloro, bromo and iodo), ether such as -OR<sup>22</sup>, thioether such as -SR<sup>22</sup> and amine such as -NR<sub>2</sub><sup>22</sup> wherein each R<sup>22</sup> is independently hydrocarbyl or substituted hydrocarbyl. In cases in which the functional group may be near a transition metal atom the functional group should not coordinate to the metal atom more strongly than the groups in those compounds are shown as coordinating to the metal atom, that is they should not displace the desired coordinating group.

By "under polymerization conditions" is meant the conditions for a polymerization that are usually used for the particular polymerization catalyst system being used. These conditions include parameters such as pressure, temperature, catalyst and cocatalyst (if present) concentrations, the type of process such as batch, semibatch, continuous, gas phase, solution or liquid slurry etc. Conditions normally done or used with the particular polymerization catalyst system, such as the use of hydrogen for polymer molecular weight control, are also considered "under polymerization conditions". Other polymerization conditions such as presence of hydrogen for molecular weight control, other polymerization catalysts, etc., are applicable with this polymerization process and may be found in the references cited herein.

By "copolymerizable olefin" is meant an olefin which, when using the particular polymerization catalyst system chosen, will copolymerize with ethylene and the acrylate ester(s) used, as well as any other comonomers present.

The steric effect of various groupings has been quantified by a parameter called E<sub>s</sub>, see R. W. Taft, Jr., J. Am. Chem. Soc., vol. 74, p. 3120-3128, and M.S. Newman, Steric Effects in Organic Chemistry, John Wiley & Sons, New York,

1956, p. 598-603. For the purposes herein, the  $E_s$  values are those for o-substituted benzoates described in these publications. If the value for  $E_s$  for any particular group is not known, it can be determined by methods described in these publications. For the purposes herein, the value of hydrogen is defined to be the same as for methyl. By a group contained within  $R^2$  having a certain  $E_s$  is meant that any portion or all of  $R^2$  may be arbitrarily chosen (this may be done multiple times), and if that portion has an  $E_s$  of about -1.0 or less, it meets this limitation. For example, if  $R^2$  was 2,4,4-trimethylpentyl (or in other words the ester was an ester of 3,5,5-trimethylhexan-1-ol), the group  $-\text{CH}_2\text{C}(\text{CH}_3)_3$  is found within 2,4,4-trimethylpentyl, and so it would meet the limitation on  $E_s$ .

Preferred transition metals herein are in Groups 3-11 and the lanthanides (IUPAC notation), more preferably Groups 8-11, and especially preferably Group 10. Specific preferred transition metals are Ni, Pd and Cu, and Ni is especially preferred.

Which catalysts will copolymerize what types of olefins are known in the art, see for instance previously incorporated US5866663 and S. D. Ittel, et al., Chem. Rev., vol. 100, p. 1169-1203 (2000) (and references cited therein), as well as WO9905189, WO9909078, WO9837110, United States Patent Application \_\_\_\_\_ (filed concurrently on 31 May 2001, Applicant's reference CL1607 US NA) (corresponding to PCT/US01/\_\_\_\_\_, filed concurrently on 31 May 2001, Applicant's reference CL1607 PCT), and United States Patent Application \_\_\_\_\_ (filed concurrently on 31 May 2001, Applicant's reference CL1655 US NA) (corresponding to PCT/US01/\_\_\_\_\_, filed concurrently on 31 May 2001, Applicant's reference CL1655 PCT), all of which are hereby incorporated by reference for all purposes as if fully set forth.

These references also give details of polymerization process conditions for such polymerizations, and reference may be had thereto for further details.

5 Examples of preferred acrylate esters of the formula  $\text{H}_2\text{C}=\text{CHC}(\text{O})\text{OR}^1$  include those wherein:

$\text{R}^1$  is  $-\text{CH}_2\text{CH}_2\text{X}$ , wherein X is hydrocarbyloxy or substituted hydrocarbyloxy, preferably aryloxy and substituted aryloxy, and especially phenoxy; or

10  $\text{R}^1$  is  $-\text{CH}_2\text{CH}_2\text{X}$ , wherein X is aryl or substituted aryl, preferably X is phenyl; or

$\text{R}^1$  is n-alkyl containing 6-12 carbon atoms, more preferably  $\text{R}^1$  is n-hexyl; or

$\text{R}^1$  is  $-\text{CH}_2\text{R}^2$  wherein  $\text{R}^2$  contains a quaternary carbon atom, more preferably  $\text{R}^2$  is 2,4,4-trimethylpentyl; or

15  $\text{R}^1$  is  $-\text{CH}_2\text{R}^2$  wherein  $\text{R}^2$  contains a group having an  $E_s$  of about -1.0 or less, more preferably about -1.5 or less, and especially preferably about -1.7 or less.

It is preferred that the copolymers described herein have the following features:

20 they contain about 1.0 to about 10 mole percent of the acrylate ester; and/or

when they are a copolymer of only ethylene and one or more acrylate esters, they have at least 10 branches of the formula  $-(\text{CH}_2)_z\text{CH}_3$ , wherein z is 0, 1, 2 or 3, present in the  
25 polymer (this is measured by  $^{13}\text{C}$  and/or  $^1\text{H}$  NMR, see for example previously incorporated US5866663 for details of how to measure branching), and more preferably there are more methyl than ethyl branches present in these branched polymers; and/or

30 when they are a copolymer of only ethylene and one or more acrylate esters, they have at least 50 branches of the formula  $-(\text{CH}_2)_z\text{CH}_3$ , wherein z is 0, 1, 2 or 3, present in the polymers (this is measured by  $^{13}\text{C}$  and/or  $^1\text{H}$  NMR, see for ex-

ample previously incorporated US5866663 for details of how to measure branching).

When  $R^1$  is  $-(CH_2CH_2)X$  or n-alkyl containing 6 or more carbon atoms, analysis of the polymer for acrylate ester homopolymer byproduct is relatively easy by  $^1H$ -NMR, since certain peaks in the NMR spectrum for homopolymer and desired copolymer are separated, see Figure 1 herein which is a  $^1H$ -NMR of such a mixture. When a more "commonly used" acrylate ester, such as methyl acrylate, is used, the peaks overlap greatly making accurate analysis impossible, as shown in Figure 2.

Besides reducing analysis costs, a quick and inexpensive analytical method allows changes to be made promptly in the polymerization process, thus ensuring more consistent product and less out of specification product to be made.

When  $R^1$  is  $-CH_2R^2$  as defined above, there is a much lower propensity to form acrylate ester homopolymer, an obvious advantage in making copolymer, since homopolymer formation is much less or nonexistent. This is illustrated in Examples 2 and 3.

The polymers of the present invention are useful as molding resins and for films. They are also (depending on their molecular weight and physical properties) useful as:

1. Tackifiers for low strength adhesives (U, vol. A1, p. 235-236) are a use for these polymers. Elastomeric and/or relatively low molecular weight polymers are preferred.

2. The polymers are useful as base resins for hot melt adhesives (U, vol. A1, p. 233-234), pressure sensitive adhesives (U, vol. A1, p. 235-236) or solvent applied adhesives. Thermoplastics are preferred for hot melt adhesives. The polymers may also be used in a carpet installation adhesive.

3. Base polymer for caulking of various kinds is another use. An elastomer is preferred. Lower molecular weight polymers are often used.

4. The polymers, particularly elastomers, may be used for modifying asphalt, to improve the physical properties of the asphalt and/or extend the life of asphalt paving, see US3980598.

5. Wire insulation and jacketing may be made from any of the polymers (see EPSE, vol. 17, p. 828-842). In the case of elastomers it may be preferable to crosslink the polymer after the insulation or jacketing is formed, for example by free radicals.

6. The polymers, especially the branched polymers, are useful as base resins for carpet backing, especially for automobile carpeting.

7. The polymers may be used for extrusion or coextrusion coatings onto plastics, metals, textiles or paper webs.

8. The polymers may be used as a laminating adhesive for glass.

9. The polymers are useful for blown or cast films or as sheet (see EPSE, vol. 7 p. 88-106; ECT4, vol. 11, p. 843-856; PM, p. 252 and p. 432ff). The films may be single layer or multilayer, the multilayer films may include other polymers, adhesives, etc. For packaging the films may be stretch-wrap, shrink-wrap or cling wrap. The films are useful for many applications such as packaging foods, geomembranes and pond liners. It is preferred that these polymers have some crystallinity.

10. The polymers may be used to form flexible or rigid foamed objects, such as cores for various sports items such as surf boards and liners for protective headgear. Structural foams may also be made. It is preferred that the

polymers have some crystallinity. The polymer of the foams may be crosslinked.

11. In powdered form the polymers may be used to coat objects by using plasma, flame spray or fluidized bed techniques.

12. Extruded films may be formed from these polymers, and these films may be treated, for example drawn. Such extruded films are useful for packaging of various sorts.

13. The polymers, especially those that are elastomeric, may be used in various types of hoses, such as automotive heater hose.

14. The polymers may be used as reactive diluents in automotive finishes, and for this purpose it is preferred that they have a relatively low molecular weight and/or have some crystallinity.

15. The polymers can be converted to ionomers, which when they possess crystallinity can be used as molding resins. Exemplary uses for these ionomeric molding resins are golf ball covers, perfume caps, sporting goods, film packaging applications, as tougheners in other polymers, and (usually extruded) detonator cords.

16. The functional groups on the polymers can be used to initiate the polymerization of other types of monomers or to copolymerize with other types of monomers. If the polymers are elastomeric, they can act as toughening agents.

17. The polymers can act as compatibilizing agents between various other polymers.

18. The polymers can act as tougheners for various other polymers, such as thermoplastics and thermosets, particularly if the olefin/polar monomer polymers are elastomeric.

19. The polymers may act as internal plasticizers for other polymers in blends. A polymer which may be plasticized is poly(vinyl chloride).

20. The polymers can serve as adhesives between other  
5 polymers.

21. With the appropriate functional groups, the polymers may serve as curing agents for other polymers with complementary functional groups (i.e., the functional groups of the two polymers react with each other).

10 22. The polymers, especially those that are branched, are useful as pour point depressants for fuels and oils.

23. Lubricating oil additives as Viscosity Index Improvers for multigrade engine oil (ECT3, Vol 14, p. 495-496) are another use. Branched polymers are preferred. Ethylene  
15 copolymer with acrylates or other polar monomers will also function as Viscosity Index Improvers for multigrade engine oil with the additional advantage of providing some dispersancy.

24. The polymers may be used for roofing membranes.

20 25. The polymers may be used as additives to various molding resins such as the so-called thermoplastic olefins to improve paint adhesion, as in automotive uses.

26. A flexible pouch made from a single layer or multi-layer film (as described above) which may be used for packaging various liquid products such as milk, or powder such  
25 as hot chocolate mix. The pouch may be heat sealed. It may also have a barrier layer, such as a metal foil layer.

27. A wrap packaging film having differential cling is provided by a film laminate, comprising at least two layers;  
30 an outer reverse which is a polymer (or a blend thereof) described herein, which contains a tackifier in sufficient amount to impart cling properties; and an outer obverse which has a density of at least about 0.916 g/mL which has

little or no cling, provided that a density of the outer reverse layer is at least 0.008 g/mL less than that of the density of the outer obverse layer. It is preferred that the outer obverse layer is linear low density polyethylene, and the polymer of the outer obverse layer have a density of less than 0.90 g/mL. All densities are measured at 25°C.

28. Fine denier fibers and/or multifilaments. These may be melt spun. They may be in the form of a filament bundle, a non-woven web, a woven fabric, a knitted fabric or staple fiber.

29. A composition comprising a mixture of the polymers herein and an antifogging agent. This composition is especially useful in film or sheet form because of its antifogging properties.

30. If the polymers are functionalized with monomers such as fluoroalkyl acrylate esters or other fluorine-containing monomers, they are useful for selectively imparting surface activity to polyolefins. This would be of use reducing fluid penetration in flash-spun polyolefin films for medical and other applications. The fluoro-functionalized polyolefins would also be useful for dispersing fluoropolymers in lubricant applications.

31. Mixtures of ethylene homopolymers or oligomers together with copolymers of ethylene and acrylates and optionally other monomers are useful as adhesion promoters, surface active agents, tougheners, and compatibilizers for adhesives.

In the above use listings, sometimes a reference is given which discusses such uses for polymers in general. All of these references are hereby included by reference. For the references, "U" refers to W. Gerhartz, et al., Ed., Ullmann's Encyclopedia of Industrial Chemistry, 5th Ed. VCH Verlagsgesellschaft mBH, Weinheim, for which the volume and

page number are given, "ECT3" refers to the H. F. Mark, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, "ECT4" refers to the J. I. Kroschwitz, et al., Ed., Kirk-Othmer Encyclopedia of Chemical Technology, 4th Ed., John Wiley & Sons, New York, for which the volume and page number are given, "EPSE" refers to H. F. Mark, et al., Ed., Encyclopedia of Polymer Science and Engineering, 2nd Ed., John Wiley & Sons, New York, for which volume and page numbers are given, and "PM" refers to J. A. Brydson, ed., Plastics Materials, 5 Ed., Butterworth-Heinemann, Oxford, UK, 1989, and the page is given.

In the Examples except where noted, all pressures are gauge pressures. In the Examples, the following abbreviations are used:

Am - amyl  
Ar - aryl  
BAF -  $B(3,5-C_6H_3-(CF_3)_2)_4^-$   
BArF -  $B(C_6F_5)_4^-$   
BHT - 2,6-di-t-butyl-4-methylphenol  
Bu - butyl  
Cmpd - compound  
E - ethylene  
EG - end-group, refers to the ester group of the acrylate being located in an unsaturated end group of the ethylene copolymer  
EGPEA - 2-phenoxyethyl acrylate  
Eoc - end-of-chain  
Equiv - equivalent  
Et - ethyl  
Ets-Bu(%) - percent of ethyl branches occurring in sec-butyl-ended branches  
GPC - gel permeation chromatography

HA - hexyl acrylate

Hex - hexyl

IC - in-chain, refers to the ester group of the acrylate being bound to the main-chain of the ethylene copolymer

Incorp - incorporation

i-Pr - iso-propyl

M.W. - molecular weight

MA - methyl acrylate

Me - methyl

MeOH - methanol

Mes-Bu(%) - percent of methyl branches occurring in sec-butyl-ended branches

MI - melt index

Mn - number average molecular weight

Mp - peak average molecular weight

Mw - weight average molecular weight

Nd - not determined

PDI - polydispersity; Mw/Mn

PE - polyethylene

PEA - 2-phenethyl acrylate

Ph - phenyl

Press - gauge pressure

RI - refractive index

Rt - room temperature

t-Bu - t-butyl

TCB - 1,2,4-trichlorobenzene

Temp - temperature

THA - 3,5,5-trimethylhexyl acrylate

TO - number of turnovers per metal center = (moles monomer consumed, as determined by the weight of the isolated polymer or oligomers) divided by (moles catalyst)

Total Me - total number of methyl groups per 1000 methylene groups as determined by  $^1\text{H}$  or  $^{13}\text{C}$  NMR analysis

UV - ultraviolet

$^1\text{H}$  NMR spectra were obtained on a 500 MHz Bruker Avance spectrometer on a 5 mm QNP probe on samples diluted ~10 mg/0.5 mL in tce-d<sub>2</sub> at 120°C using a 90 degree pulse of 14  $\mu\text{sec}$ , a spectral width of 12.8 kHz, an acquisition time of 2.6 sec and a recycle delay of 30 sec. A total of 8 transients were acquired. Spectra were referenced to tce-d<sub>2</sub> at 5.928 ppm. Unique peaks in each spectrum from the different types of comonomer signals, for example from 4.25 to 4.55 ppm for the Ethylene/Ethylene glycol phenyl ether acrylate copolymer, and also the PE signals in the region 0.6-2.0 ppm, were carefully integrated and the results used to calculate mole% acrylate incorporation.

Total methyls per 1000  $\text{CH}_2$  are measured using different NMR resonances in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Because of accidental overlaps of peaks and different methods of correcting the calculations, the values measured by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy will not be exactly the same, but they will be close, normally within 10-20% at low levels of acrylate comonomer. In  $^{13}\text{C}$  NMR spectra, the total methyls per 1000  $\text{CH}_2$  are the sums of the  $1\text{B}_1$ ,  $1\text{B}_2$ ,  $1\text{B}_3$ , and  $1\text{B}_{4+}$ , EOC resonances per 1000  $\text{CH}_2$ , where the  $\text{CH}_2$ 's do not include the  $\text{CH}_2$ 's in the alcohol portions of the ester group. The total methyls measured by  $^{13}\text{C}$  NMR spectroscopy do not include the minor amounts of methyls from the methyl vinyl ends nor the methyls in the alcohol portion of the ester group. In  $^1\text{H}$  NMR spectra, the total methyls are measured from the integration of the resonances from 0.6 to 1.08 ppm and the  $\text{CH}_2$ 's are determined from the integral of the region from 1.08 to 2.49 ppm. It is assumed that there is 1 methine for every methyl group, and 1/3 of the methyl integral is subtracted from the

methylene integral to remove the methine contribution. The methyl and methylene integrals are also usually corrected to exclude the values of the methyls and methylenes in the alcohol portion of the ester group, if this is practical. Because of the low levels of incorporation, this is usually a minor correction. Corrections are also made to exclude any contributions from acrylate homopolymer to the methyl or methylene integrals in both the  $^{13}\text{C}$  and  $^1\text{H}$  spectra where this is warranted.

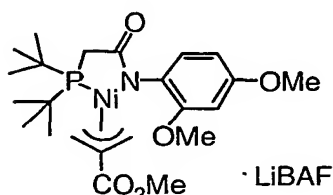
10 General Information Regarding Molecular Weight Analysis:

GPC molecular weights are reported versus polystyrene standards. Unless noted otherwise, GPC's were run with RI detection at a flow rate of 1 mL/min at 135 °C with a run time of 30 min. Two columns were used: AT-806MS and WA/P/N 34200. A Waters RI detector was used and the solvent was TCB with 5 grams of BHT per gallon. Dual UV/RI detection GPC was run in THF at rt using a Waters 2690 separation module with a Waters 2410 RI detector and a Waters 2487 dual absorbance detector. Two Shodex columns, KF-806M, were used along with one guard column, KF-G.

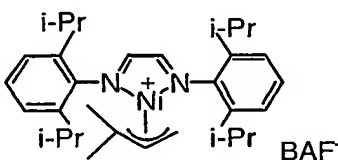
In addition to GPC, molecular weight information was at times determined by  $^1\text{H}$  NMR spectroscopy (olefin end group analysis) and by melt index measurements (g/10 min at 190°C).

25 General Procedure A for Ethylene Polymerizations and Co-polymerizations: In a nitrogen-filled drybox, a 40 mL glass insert was loaded with the nickel compound and, optionally, a Lewis acid (e.g.,  $\text{BPh}_3$  or  $\text{B}(\text{C}_6\text{F}_5)_3$ ) and borate (e.g.,  $\text{NaBAF}$  or  $\text{LiBArF}$ ), and any other specified cocatalysts and other additives. Next, the solvent was added to the glass insert followed by the addition of any co-solvents and then comonomers. The insert was greased and capped. The glass insert was then loaded in a pressure tube inside the drybox. The

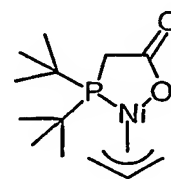
pressure tube was then sealed, brought outside of the dry-box, connected to the pressure reactor, placed under the desired ethylene pressure and shaken mechanically. After the stated reaction time, the ethylene pressure was released and the glass insert was removed from the pressure tube. The polymer was precipitated by the addition of MeOH (~20 mL). The polymer was then collected on a frit and rinsed with MeOH and, optionally, acetone. The polymer was transferred to a pre-weighed vial and dried under vacuum overnight. The polymer yield and characterization were then obtained.



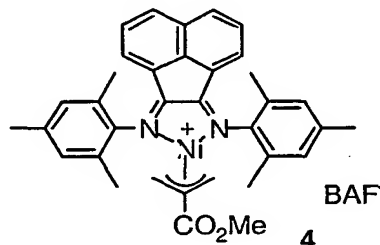
1



2



3



4

#### Examples 1-5

Examples 1-5 are listed in Tables 1 and 2 below. Figures for compounds 1 through 4 are shown above. The polymerizations were carried out according to General Procedure A. Varying amounts of acrylate homopolymer are present in the isolated polymers. In Table 1, the yield of the polymer is reported in grams and includes the yield of the dominant ethylene/acrylate copolymer as well as the yield of any acrylate homopolymer that was formed. Molecular weights were determined by GPC, unless indicated otherwise. Mole percent acrylate incorporation and total Me were determined by  $^1\text{H}$  NMR spectroscopy, unless indicated otherwise. Mole percent ac-

rylate incorporation is typically predominantly IC, unless indicated otherwise.

Table 1

E/Acrylate Copolymerizations (6.9 MPa E, 120 °C, 18 h)

| Ex             | Cmpd (mmol) | Acrylate mL (Solvent mL) | B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (Borate equiv) | Yield <sup>a</sup> g | Acrylate Incorp. mol%   | M.W.   | Total Me                | Homopolymer <sup>b</sup> g ( <sup>13</sup> C NMR) |
|----------------|-------------|--------------------------|---|----------------------|-------------------------|--|-------------------------|---|
| 1              | 1 (0.02)    | EGPEA 2 (p-Xylene 8)     | 20 equiv (NaBAF1 0)   | 8.06                 | 1.5<br>0.7 IC<br>0.8 EG | M <sub>p</sub> =3,098;<br>M <sub>w</sub> =3,461;<br>M <sub>n</sub> =1,122;<br>PDI=3.09   | 22.3                    | —   |
| 2              | 2 (0.02)    | EGPEA 2 (TCB 8)          | 40 equiv (None)   | 2.17                 | 0.03 ( <sup>13</sup> C) | M <sub>p</sub> =12,550;<br>M <sub>w</sub> =13,744;<br>M <sub>n</sub> =5,936;<br>PDI=2.32 | Nd                      | 0.031 g (1.43% of total yield)                    |
| 3 <sup>e</sup> | 2 (0.02)    | THA 2 (TCB 8)            | 40 equiv (None)   | 2.37                 | 0.23 ( <sup>13</sup> C) | M <sub>p</sub> =12,775;<br>M <sub>w</sub> =13,777;<br>M <sub>n</sub> =7,165;<br>PDI=1.92 | 43.1 ( <sup>13</sup> C) | Not detected                                      |
| 4              | 3 (0.02)    | HA 4 (TCB 6)             | 40 equiv (None)   | 2.09 <sup>c</sup>    | 4.0<br>2.2 IC<br>1.8 EG | M <sub>p</sub> =931;<br>M <sub>w</sub> =1,399;<br>M <sub>n</sub> =856;<br>PDI=1.63       | 54                      | —   |
| 5 <sup>d</sup> | 4 (0.0019)  | PEA 1 (TCB 9)            | 211 equiv (NaBAF 105)   | 0.043                | 1.4                     | M <sub>p</sub> =6,238;<br>M <sub>w</sub> =8,319;<br>M <sub>n</sub> =4,238;<br>PDI=1.96   | 44.4                    | —   |

<sup>a</sup>Yield of copolymer and homopolymer. <sup>b</sup>Yield of homopolymer as determined from <sup>13</sup>C NMR integration; <sup>c</sup>T<sub>m</sub> = 108 °C (191.4 J/g); <sup>d</sup>In the <sup>1</sup>H NMR spectrum in TCE-d<sub>2</sub> (referenced to the residual protons of TCE; 500 MHz), the chemical shift of the -C(O)OCH<sub>2</sub>- triplet of the ethylene/PEA copolymer occurs at 4.34 ppm, whereas the chemical shift of the broad -C(O)OCH<sub>2</sub>- resonance of the homopolymer occurs at 4.29 ppm, for a separation of 0.05 ppm. For comparison, the separations of the -C(O)OCH<sub>2</sub>- resonances of the copolymers (IC resonance) and homopolymers of HA and EGPEA shown in the figures herein are approximately 0.03 ppm and 0.08 ppm, respectively; <sup>e</sup>For rapid analysis purposes, in the <sup>1</sup>H NMR spectrum of the ethylene/THA copolymer in TCE-d<sub>2</sub> (referenced to the residual protons of TCE; 500 MHz), the chemical shift of the -C(O)OCH<sub>2</sub>- triplet occurs at 4.16 ppm.

Table 2

<sup>13</sup>C NMR Branching Analysis for THA Copolymer of Example 3

| Total Me | Me   | Et  | Pr  | Bu  | Hex+ & eoc | Am+ & eoc | Bu+ & eoc | Me <sub>3</sub> -Bu (%) | Et <sub>3</sub> -Bu (%) |
|----------|------|-----|-----|-----|------------|-----------|-----------|-------------------------|-------------------------|
| 43.1     | 29.0 | 4.4 | 2.1 | 1.7 | 3.8        | 7.5       | 7.6       | 2.3                     | 15.1                    |

## CLAIMS

What is claimed is:

1. A process for the manufacture of a copolymer, comprising the step of contacting, under polymerization conditions, a monomer component comprising ethylene and one or more acrylate esters, and a polymerization catalyst system containing a transition metal, characterized in that said one or more acrylate esters comprises a compound of the formula  $\text{H}_2\text{C}=\text{CHC}(\text{O})\text{OR}^1$ , wherein:
  - 10  $\text{R}^1$  is  $-\text{CH}_2\text{CH}_2\text{X}$ , an n-alkyl containing 6 or more carbon atoms, or  $-\text{CH}_2\text{R}^2$ ;  
 $\text{X}$  is aryl, substituted aryl, hydrocarbyloxy, substituted hydrocarbyloxy, fluoro or fluoroalkyl; and  
 $\text{R}^2$  is an alkyl containing at least one quaternary carbon atom, or having a grouping within  $\text{R}^2$  having an  $\text{E}_s$  of about  
15 -1.0 or less, or both.
2. The process of claim 1, characterized in that  $\text{X}$  is hydrocarbyloxy or substituted hydrocarbyloxy.
- 20 3. The process of claim 1, characterized in that  $\text{X}$  is aryloxy or substituted aryloxy.
4. The process of claim 1, characterized in that  $\text{X}$  is  
25 aryl or substituted aryl.
5. The process of claim 1, characterized in that  $\text{R}^1$  is n-alkyl containing 6 to 12 carbon atoms.
- 30 6. The process of claim 1, wherein  $\text{R}^1$  is  $-\text{CH}_2\text{R}^2$ .
7. The process of claim 1, characterized in that said transition metal is nickel, palladium or copper.

8. A copolymer of ethylene, one or more acrylate esters and, optionally, one or more other copolymerizable monomers, characterized in that said acrylate esters are about 0.1 to  
5 about 30 mole percent of the total number of all repeat units in said copolymer, and that said one or more acrylate esters comprises a compound of the formula  $H_2C=CHC(O)OR^1$ , wherein:

$R^1$  is  $-(CH_2CH_2)X$ , n-alkyl containing 6 or more carbon  
10 atoms, or  $-CH_2R^2$ ;

X is aryl, substituted aryl, hydrocarbyloxy, substituted hydrocarbyloxy, fluoro, or fluoroalkyl; and

$R^2$  is alkyl containing at least one quaternary carbon atom, or having a grouping within  $R^2$  having an  $E_s$  of about  
15 -1.0 or less, or both.

9. The copolymer of claim 8, characterized in that X is hydrocarbyloxy or substituted hydrocarbyloxy.

20 10. The copolymer of claim 8, characterized in that X is aryloxy or substituted aryloxy.

11. The copolymer of claim 8, characterized in that X is aryl or substituted aryl.

25

12. The copolymer of claim 8, characterized in that  $R^1$  is n-alkyl containing 6 to 12 carbon atoms.

13. The copolymer of claim 8, characterized in that  $R^1$   
30 is  $-CH_2R^2$ .

14. The copolymer of any one of claims 8-13, characterized in that ethylene and said one or more acrylate esters are essentially the only monomers present.

5        15. The copolymer of claim 14, characterized in that said copolymer has at least 10 branches of the formula  $-(CH_2)_zCH_3$ , wherein z is 0, 1, 2 or 3.

10       16. The copolymer of claim 15, characterized in that there are more methyl branches than ethyl branches in said copolymer.

15       17. The copolymer of claim 14, characterized in that said copolymer has at least 50 branches of the formula  $-(CH_2)_zCH_3$ , wherein z is 0, 1, 2 or 3.

1/3

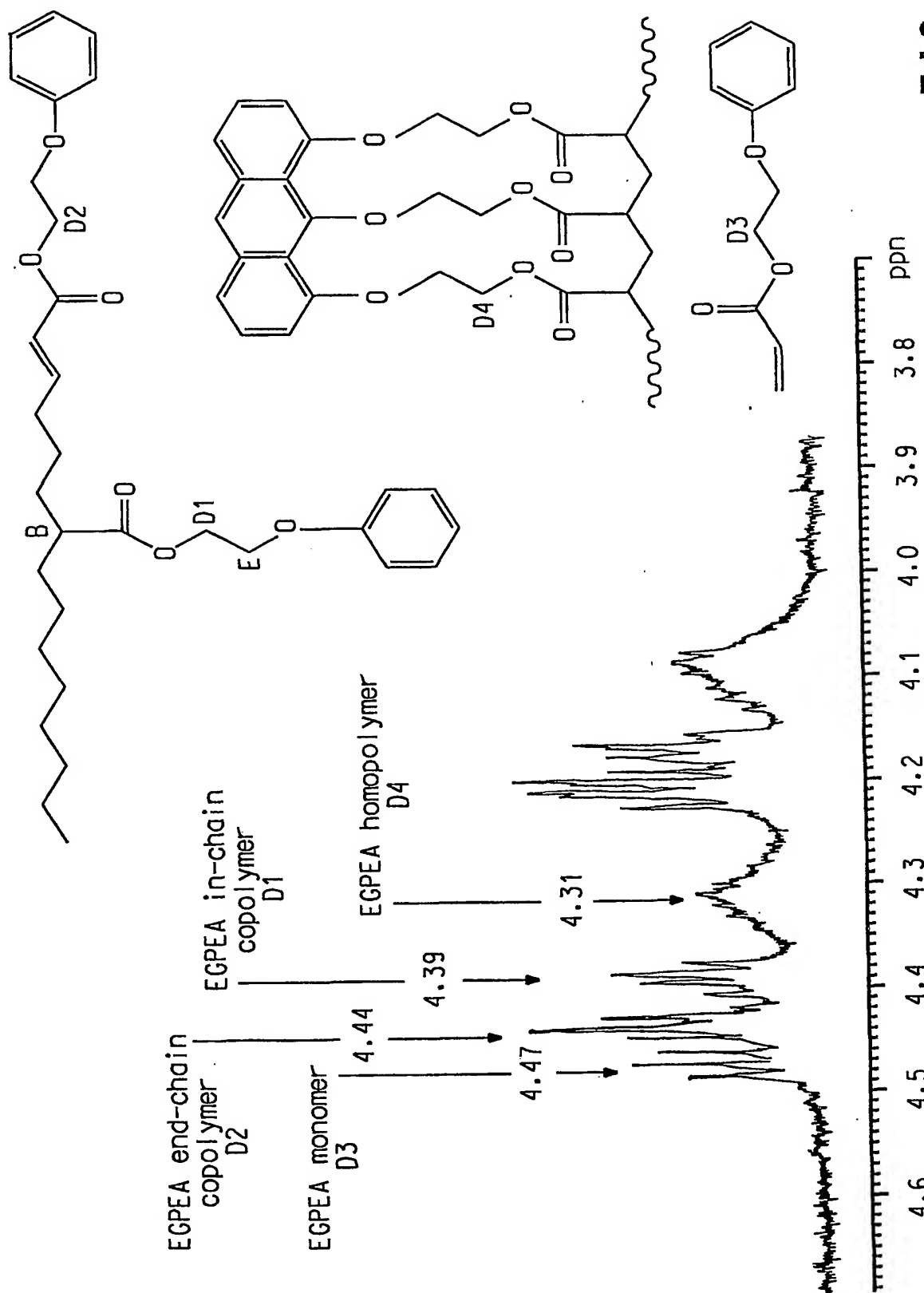


FIG. 1

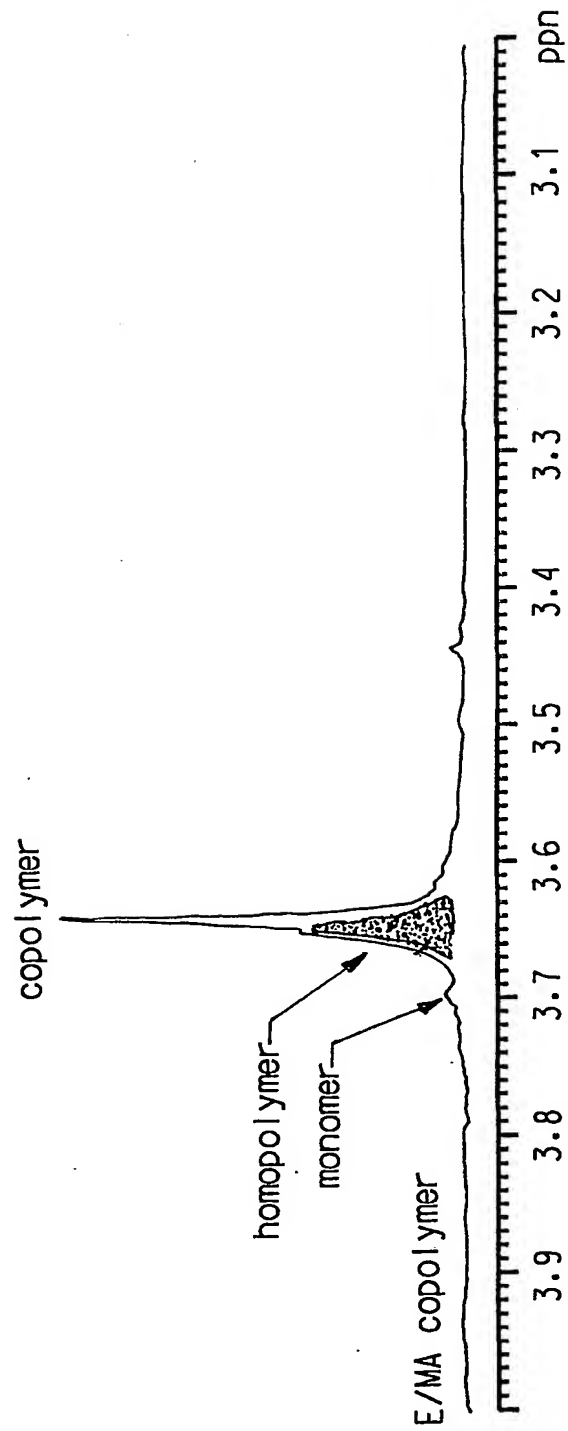


FIG. 2

3/3

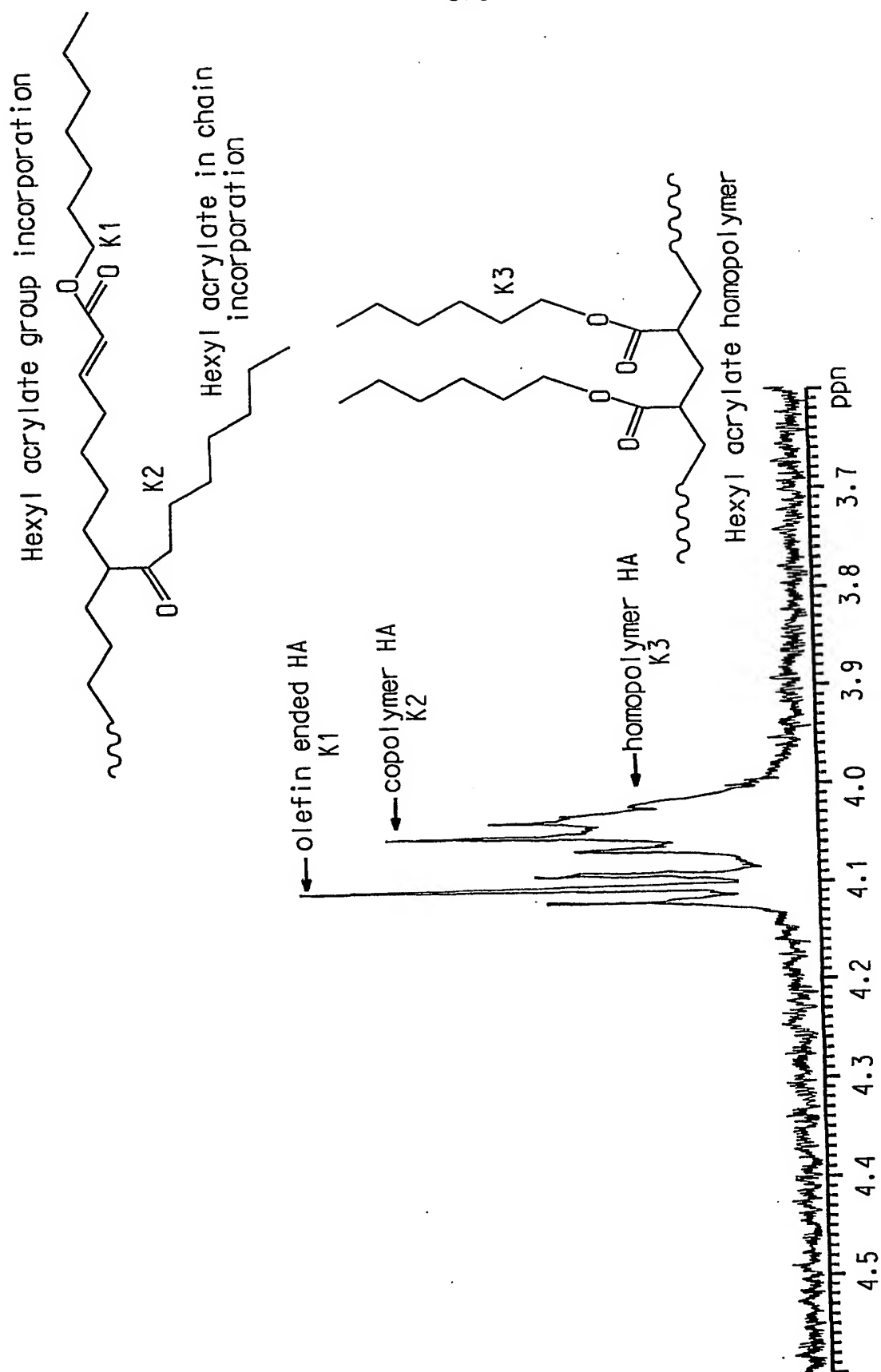


FIG. 3



(43) International Publication Date  
6 December 2001 (06.12.2001)

PCT

(10) International Publication Number  
**WO 01/092354 A3**

- (51) International Patent Classification<sup>7</sup>: **C08F 210/02**, 4/70 // (C08F 210/02, 220:18, 220:30)
- (21) International Application Number: PCT/US01/17626
- (22) International Filing Date: 31 May 2001 (31.05.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
- |            |                              |    |
|------------|------------------------------|----|
| 60/208,087 | 31 May 2000 (31.05.2000)     | US |
| 60/211,601 | 15 June 2000 (15.06.2000)    | US |
| 60/214,036 | 23 June 2000 (23.06.2000)    | US |
| 60/264,537 | 25 January 2001 (25.01.2001) | US |
- (71) Applicant (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **JOHNSON, Lynda, K.** [US/US]; 707 Burnley Road, Wilmington, DE 19803 (US). **WANG, Lin** [US/US]; 112 Brook Run, Hockessin, DE 19707 (US). **MCCORD, Elizabeth, F.** [US/US]; 514 Hemlock Drive, Hockessin, DE 19707 (US).
- (54) Title: COPOLYMERS OF ETHYLENE AND SELECTED ACRYLATE ESTERS
- (57) Abstract: In the copolymerization of ethylene and acrylate esters, the use of selected acrylate esters suppresses the formation of acrylate ester homopolymer, and/or allows the rapid analysis by <sup>1</sup>H-NMR of the amount of homopolymer by product present in the copolymer, both aids in manufacturing high quality copolymers. Useful such acrylates include hexyl acrylate, 3,5,5-trimethylhexyl acrylate, 2-phenoxyethyl acrylate and 2-phenylethyl acrylate. The polymers are useful for films and molding resins.
- (74) Agent: **LERMAN, Bart, E.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:  
— with international search report
- (88) Date of publication of the international search report:  
16 January 2003
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/092354 A3

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/JP 01/17626

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C08F210/02 C08F4/70 //(C08F210/02,220:18,220:30)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, CHEM ABS Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|------------|--|-----------------------|
| X          | WO 99 30822 A (EXXON RESEARCH ENGINEERING CO) 24 June 1999 (1999-06-24)<br>page 11, paragraph 2<br>examples 17,21<br>----- | 1,5,7                 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

26 April 2002

Date of mailing of the international search report

14. 08. 2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Parry, J

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-17 (in part)

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-17 (in part)

The subject matter of claims 1-17, insofar as it relates to the formula of claim 1 and 8 wherein  $R1 = CH_2CH_2X$ ,  $X = \text{aryl}$  or substituted aryl.

2. Claims: 1-17 (in part)

The subject matter of claims 1-17, insofar as it relates to the formula of claim 1 and 8 wherein  $R1 = CH_2CH_2X$ ,  $X = \text{hydrocarbyloxy}$  or substituted hydrocarbyloxy.

3. Claims: 1-17 (in part)

The subject matter of claims 1-17, insofar as it relates to the formula of claim 1 and 8 wherein  $R1 = CH_2CH_2X$ ,  $X = \text{fluoro}$  or fluoroalkyl.

4. Claims: 1-17 (in part)

The subject matter of claims 1-17, insofar as it relates to the formula of claim 1 and 8 wherein  $R1 = \text{an n-alkyl}$  containing 6 or more carbon atoms.

5. Claims: 1-17 (in part)

The subject matter of claims 1-17, insofar as it relates to the formula of claim 1 and 8 wherein  $R1 = CH_2R_2$ , with  $R_2 = \text{an alkyl}$  containing at least one quaternary carbon atom.

6. Claims: 1-17 (in part)

The subject matter of claims 1-17, excluding the subject matter of groups 1-5 above, insofar as it relates to the formula of claim 1 and 8 wherein  $R1 = CH_2R_2$ , with  $R_2 = \text{an...}$  Es of about -1.0 or less.

| Patent document<br>cited in search report |   | Publication<br>date |    | Patent family<br>member(s) | Publication<br>date |
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|   |   |                     | EP | 1017491 A1                 | 12-07-2000          |
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|   |   |                     | US | 6037297 A                  | 14-03-2000          |
|   |   |                     | US | 6180788 B1                 | 30-01-2001          |
|   |   |                     | US | 6417303 B1                 | 09-07-2002          |
| -----                                     |   |                     |    |                            |                     |

Form PCT/SA/210 (patent family annex) (July 1992)

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